MICROWAVE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION OF DIAMOND IN THE VAPOR OF METHANOL-BASED LIQUID SOLUTIONS

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ABSTRACT

A method for depositing diamond crystals and diamond films from methanol-based liquid solutions is reported. Liquid solutions are prepared by mixing methanol with other carbon containing liquid compounds which contain a greater than one ratio of carbon to oxygen such as acetone, ethanol, and iso-propanol. An electrical discharge is generated by microwave power in a metal cavity in order to dissociate the vapor mixture from one of the liquid solutions, from which radicals such as OH, O, and H that etch non-diamond carbon much faster than diamond, as well as carbon containing radicals such as CH_3 are produced on and near a substrate surface. Graphitic, amorphous and other forms of non-diamond carbon deposits are either suppressed from being deposited on the substrate or preferentially etched by OH, O, and H radicals resulting in the deposition of high quality diamond crystals and diamond films without the need for compressed gases such as hydrogen and methane.

1. INTRODUCTION

Diamonds that are synthesized by means of chemical vapor deposition has many unique and outstanding properties that make it an ideal material for a broad range of scientific and technological applications [1]. A number of methods for chemical vapor deposition of diamond based on varied gas mixtures and energy sources for dissociating the gas mixture have been reported [2]. These techniques include the use of high-temperature electrons in various kinds of plasmas, high-temperature surfaces of hot filaments, and high-temperature gases in combustion flames to dissociate molecular hydrogen, oxygen, halogen, hydrocarbon, and many other carbon containing gases. The substrate is usually maintained at a temperature much lower than that of electrons in a plasma, the hot filaments, or the combustion flame, resulting in a super equilibrium of atomic hydrogen near the diamond growing surface.

Atomic hydrogen is believed to be crucial in the diamond chemical vapor deposition (CVD) process because of its effectiveness of stabilizing the growing surface of diamond at the CVD temperature and pressure that is thermodynamically in favor of the growth of graphite instead of diamond. Almost every reported diamond chemical vapor deposition process, therefore, involves the use of hydrogen gas or some kind of hydrogen containing molecules. The most typical diamond CVD process uses methane gas diluted by 94-99.9% hydrogen. The super equilibrium of atomic hydrogen can be achieved in a gas mixture with varied percentage of molecular hydrogen depending on the balance between the effectiveness of the dissociation process in generating atomic hydrogen and the loss processes for atomic hydrogen to recombine or react with other radicals. By the use of a high-power-density microwave plasma, atomic hydrogen is very effectively generated from molecular hydrogen and diamond can be deposited in a mixture of methane diluted by less than 50% hydrogen [3] Growth of diamond from oxy-acetylene flames uses acetylene and oxygen with the ratio of acetylene to oxygen slightly greater than 1 without needing molecular hydrogen. Diamond is deposited in the reducing "inner flame" where atomic hydrogen is produced by the high temperature flame as one of the burn products. In addition to atomic hydrogen, there is plenty of OH radicals present near the diamond growing surface inside the flame.

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Microwave plasma was applied to convert the vapor of methanol-based liquid solutions into favorable mixtures of species for diamond nucleation and growth without any addition of compressed gases. Diamond of excellent quality has been deposited on various substrates including metals, semiconductors, and insulators in a wide temperature range. This liquid only process is economic, safe and may replace the most popularly applied hydrogen/ methane diamond growth process for mass production of CVD diamond.

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OH and O radicals can play another role of atomic hydrogen in the diamond growth process, i.e., preferential etching of non-diamond carbon resulting in a net deposition of high purity diamond. Small quantity of oxygen (0.5-2%) or water vapor (<6%) added to the methane and hydrogen mixture has been reported to improve diamond crystallinity and to lower the diamond deposition temperature [4,5] The quantity of oxygen and water in a feedstock is a relative term depending on other process parameters. Diamond has been grown in a microwave plasma of acetone/oxygen mixture with molecular ratio near 1:1 [6].

Most of diamond CVD processes involve in the use of one or more compressed gases. The most typical example is the use of 1% methane gas diluted by 99% hydrogen. These gases usually must be precisely controlled using electronic mass flow controllers to ensure an accurate composition in the gas feed. Rudder et al. reported the success in the growth of diamond using an RF plasma in a mixture of water (more than 40%) and alcohol [7]. No compressed gases were needed for this diamond deposition process. Rudder et al., in their comparative example 6 , also concluded that the hot-filament assisted CVD process using 18 sccm water and 40 sccm ethanol at 80 Torr with filament temperature at 2100°C located about 2 mm from the silicon substrate at 650°C deposited only fine grain graphite in contrary to the deposition of diamond as claimed by Komaki et al. [8].

In a typical electrical discharge such as a microwave plasma, there are abundant electrons with an average temperature exceeding 10,000°C. These energetic electrons effectively dissociate molecular species and generate high concentrations of radicals that are necessary for the deposition of diamond and the preferential etching of non-diamond deposits without needing a high temperature filament. Although electrons are very hot, they do not heat the substrate and reactor walls to as high as their temperatures because electrons have small weight and small heat capacity. Ions and the most of abundant neutral species in a typical non-thermal plasma are much cooler than electrons. Because of the non-equilibrium nature of this kind of plasmas and the availability of very hot electrons, the process parameter window for successful deposition of diamond using a methanol-based liquid solution is much wider than that for a hot-filament assisted CVD technique. After fine tuning the process conditions, diamond films have been deposited in our laboratory by means of hot-filament assisted CVD technique in the vapor of methanol-based solutions. The process and results are being reported in a separate paper.

2. EXPERIMENTAL

A method of synthesizing diamond economically using a liquid solution as the feedstock and an electrical discharge as the means of dissociating and reacting the vapor of the solution is reported. A solution consisting of 50-98% by weight of methanol and 2-50% by weight of selected carbon containing compounds such as ethanol, isopropanol, and acetone are premixed and fed into a deposition chamber through a liquid flow controller such as a needle valve. The solution vaporizes as it enters the low pressure deposition chamber. The vapor consists of the same composition as the solution. When the vapor passes through an electrical discharge zone, it is dissociated to generate OH, H, O, CH_3 and other carbon containing radicals.

The substrate is a sheet or a wafer of silicon, copper, aluminum and molybdenum. Some of the substrates are polished using 1um diamond paste prior to the deposition process. The substrate can be either in touch with the plasma or at a distance from the plasma. The substrate holder is water cooled to control the temperature of the substrate. In the following experiments, substrates were in touch with a microwave plasma generated inside a cylindrical microwave cavity. The reactor chamber pressure was maintained between 10 and 250 torr. A substrate of about 2.5cm by 2.5cm in size was heated by the plasma to about 500-1600°C as measured by a dual color optical pyrometer. Diamond was grown at a rate of 0.5-20 um per hour depending on the composition of the solution, the vapor pressure, the substrate temperature, and the plasma power density.

Figure 1 illustrates the microwave enhanced chemical vapor deposition system. As illustrated in Fig. 1, a premixed solution **5** is fed from the solution container **4** by a teflon or metal tubing **6** through a liquid flow controller (for example, a needle valve **7**) to the inlet **2** of a stainless steel reactor chamber **1** that is typically of 6" in diameter. When the liquid solution enters the low pressure side of the needle

valve, it vaporizes to form a vapor mixture with the same molar composition as the pre-mixed solution. In addition to the inlet **2**, the reactor chamber has an outlet **3** connected to a mechanical vacuum pump (not shown) through an automatically controlled throttle valve (not shown) to maintain constant pressure throughout the deposition process, for circulating the vapor of the methanol-based vapor through the reactor chamber. The vapor is maintained at a pressure within the vacuum chamber of between 1 and 250 torr, with the pressure being monitored by a pressure gauge (not shown).

Microwave power **8** is applied to the reactor chamber which is part of the cylindrical cavity for the microwave of 2.45 GHz through a quartz window **9** that separate the low pressure reactor form the ambient pressure. A substrate **11** was placed on a water cooled substrate holder **12** with its temperature monitored by a dual color optical pyrometer (not shown). The microwave plasma **10** dissociates methanol-based vapor and releases OH, H, O, CH_3, CH_2, ...etc. radicals for a net deposition of diamond on the silicon surface. Methanol vapor, of which the chemical symbol is CH_3OH, has the carbon to oxygen ratio being equal to one. When it is dissociated, it forms so much oxidizing radicals that diamond grows at a low rate. When a proper quantity of a carbon containing compound, such as ethanol, isopropanol and acetone, with carbon to oxygen ratio higher than that of methanol is added to the solution, diamond growth rate increases rapidly. Ethanol, of which the chemical symbol is CH_3CH_2OH, has the carbon to oxygen ratio of 2. Isopropanol, of which the chemical symbol is $(CH_3)_2CHOH$, has the carbon to oxygen ratio of 3. Acetone, of which chemical symbol is CH_3COCH_3, has the carbon to oxygen ratio of 3. The deposition process lasted for 2-100 hours resulting in diamond films with well faceted diamond grains clearly visible using an optical microscope. The diamond grain size ranges from sub-micrometers to more than 500 um.

Substrates of silicon, copper, aluminum and molybdenum were cleaned by acetone and methanol before being loaded onto the substrate holder. Some substrates were polished with diamond paste containing 1 um size diamond particles. The typical deposition parameters are summarized as follows: Microwave power, 600-3000W; Vapor pressure, 10-250Torr; Substrate temperature, 500-1600°C; Methanol, 50-98% by weight; Ethanol, isopropanol, and acetone, 2-50% by weight.

A phase-contrast optical microscope was used to examine the crystal shapes and surface morphology of the deposited films. Diamond grains with (100) or (111) facets can clearly be seen using this optical microscope. The film thickness can also be measured by examining the cross-sectional view of the films using the optical microscope. A micro Raman spectrometer powered by an Argon ion laser was used to examine the phase purity of the deposited films. Diamond peak around 1332 cm^{-1} provides us with a convincing evidence that the deposited carbon films are diamond.

3. RESULTS AND DISCUSSION

When methanol alone was used as the feedstock, too much oxidizing and carbon etching radicals were generated resulting in a very slow growth rate of diamond. For example, when 2000W microwave was applied at a pressure of 80 torr and a substrate temperature of 900° C, the methanol plasma deposited only about 2 um diamond on a molybdenum substrate after 40 hours of deposition.

A liquid solution consisting of 4.6 grams of ethanol and 100 grams of methanol was used as the feedstock. A molybdenum plate of ½ inch thick and 2 inches in diameter was polished by diamond paste containing 1um sized diamond powder and cleaned by acetone and methanol. Microwave power of 2kW was applied at the vapor pressure of 80 Torr resulting in the substrate being heated to 1000°C. After 45 hours of deposition, the film separated by itself from the molybdenum and was about 45 um in thickness. The growth rate was about 1 um per hour. Diamond growth rate increases with increasing quantity of ethanol in the methanol-based solution. Figure 2 shows the optical micrograph of a free-standing diamond film. The diamond peak at 1332 cm^{-1} in the Raman spectrum shown in Figure 3 indicates that the diamond film is of very good quality. Similar results were obtained with solutions containing acetone and methanol and solutions containing isopropanol alcohol and methanol.

4. SUMMARY

A microwave plasma enhanced chemical vapor deposition technique using methanol-based solutions as the feedstock has been developed for the deposition of diamond crystals and diamond films. The OH, H, and O radicals generated by the dissociation of the methanol-based vapor were proven to be sufficient in suppressing the growth of graphitic, amorphous and other non-diamond carbon resulting in the deposition of high quality diamond. By the addition to methanol with carbon containing compounds that contain more carbon than oxygen, the diamond growth rate increases significantly.

The methanol-based solution is less expensive than typical compressed gases that have been used for diamond deposition. The mixing of the methanol-based solutions can be easily performed making it unnecessary to use expensive precision electronic mass flow controllers to ensure accurate vapor compositions. This method of diamond deposition is reasonably safe and may be one of the most economic ways of manufacturing CVD diamond.

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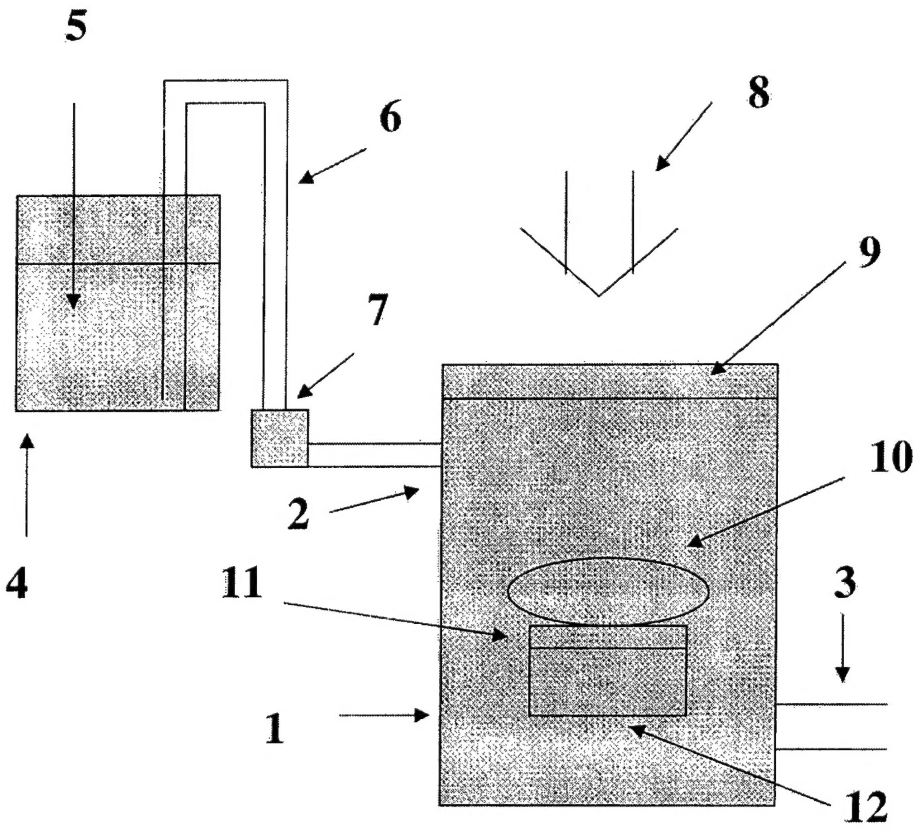

Figure 1. Microwave plasma enhanced CVD apparatus.

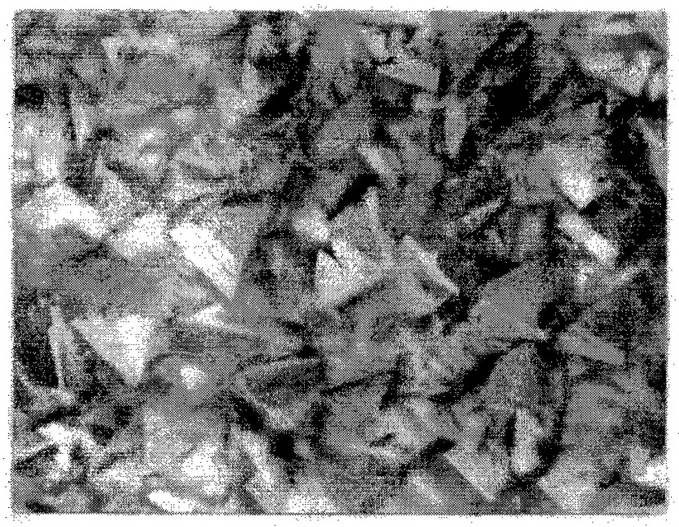

Figure 2. Optical micrograph of a diamond film deposited in the vapor of a solution consisting of 4.6 grams of ethanol and 100 grams of methanol.

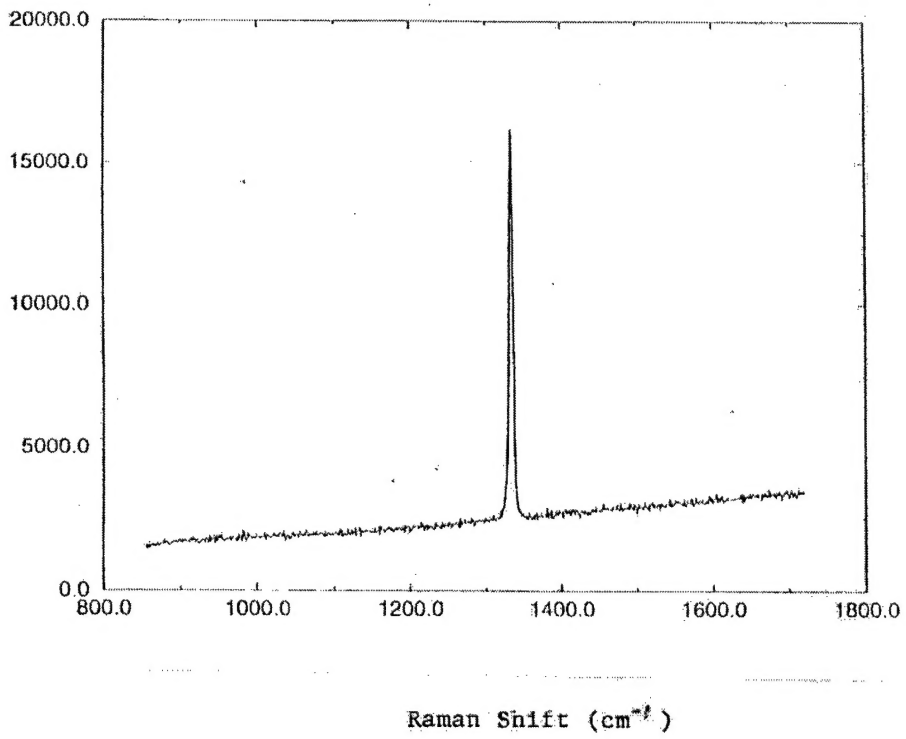

Figure 3. Raman spectrum of the diamond film shown in Figure 2.